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Chemical Compatibility Issues Related to Use of Copper as an Interfacial Layer for SiC Fiber Reinforced Ti_3Al+Nb Composite

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CHEMICAL COMPATIBILITY ISSUES RELATED TO USE OF COPPER AS AN INTERFACIAL LAYER FOR SiC FIBER REINFORCED Ti₃Al+Nb COMPOSITE

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ABSTRACT

Reaction of Cu, a potential interfacial compliant layer for the Ti₃Al+Nb/SiC composite, with SiC, SCS-6 fiber, and the Ti₃Al+Nb matrix was examined at two temperatures: 1223 and 1273 K. Reaction of Cu with SiC resulted in the formation of a Cu-Si solution and free carbon, the reaction product being molten at 1273 K. Hot pressing the SCS-6 fiber in a Cu matrix at 1273 K resulted in cracking and delamination of the outer carbon-rich coating, thus allowing Cu to penetrate to the SiC-carbon coating interface and react with SiC. In contrast, no such damage to the outer coating was observed at 1223 K. There was excessive reaction between Cu and the Ti₃Al+Nb matrix, the reaction product being molten both at 1223 and 1273 K. An interlayer of Nb between Cu and Ti₃Al+Nb matrix prevented the reaction between the two.

INTRODUCTION

Continuous fiber reinforced titanium aluminides based on the Ti₃Al (α_2) phase are currently being considered as compressor materials in gas turbine engines intended for future aerospace applications. Because SiC is one of the few fibers currently available, current research efforts are directed towards developing Ti₃Al-based composites using this fiber.

There is, however, a major problem with the SiC fiber reinforced Ti₃Al composite. Because the coefficient of thermal expansion (CTE) of SiC ($4-5 \times 10^{-6} \text{ K}^{-1}$) is considerably lower than that of the matrix ($\sim 10-11 \times 10^{-6} \text{ K}^{-1}$), residual tensile hoop stresses will develop in the matrix after cooling of the composite from processing temperature, which is in the range of 1273 to 1373 K, to room temperature. These residual stresses, if large enough, can cause cracking of the matrix. Indeed, radial cracks have been observed (ref. 1) in the matrix near the fiber-matrix interface for a Ti₃Al+Nb*/SiC composite after cooling from the processing temperature. These radial cracks further propagate (ref. 1) under thermal cycling conditions and thus reduce the useful life of the composite.

* Ti₃Al+Nb refers to Ti-24Al-11Nb (at. %) alloy.

One approach in accommodating the CTE mismatch between the fiber and the matrix consists of inserting an interfacial layer, known as a compliant layer, between the fiber and the matrix so as to reduce or eliminate the residual stresses in the matrix. The required characteristics of this interfacial compliant layer for a $\text{Ti}_3\text{Al+Nb/SiC}$ composite have recently been derived by Arnold et al. (ref. 2) from micromechanics considerations. Based on this study Cu appears to be the best choice as a compliant layer among pure metals.

Copper, in order to be effective as a compliant layer, must be chemically stable in the composite. This paper addresses the issues related to the chemical compatibility of Cu with SiC fibers as well as with the $\text{Ti}_3\text{Al+Nb}$ matrix.

EXPERIMENTAL

Materials: Oxygen-free high conductivity (OFHC) Cu was used in this study. Silicon carbide used in this study include both fibers and plates. Chemically vapor deposited (CVD) SiC fibers were obtained from Textron Specialty Materials, Inc., Lowell, MA. Two different types of fibers were used in this study; one has a double layer of outer carbon-rich coating (SCS-6 fiber) and the other has no coating (SCS-0). Chemically vapor deposited SiC plates were obtained from CVD Inc., Woburn, MA. The $\text{Ti}_3\text{Al+Nb}$ alloy was prepared by hot pressing and HIPing of alloy powder.

Reaction studies: Reaction of Cu with SiC fibers was studied by hot pressing a single SiC fiber between two Cu disks under a vacuum of 10^{-5} atm. The applied pressure was in the range of 10 to 20 MPa. Two hot pressing temperatures were employed: 1273 and 1223 K. Reaction studies with SiC plates and $\text{Ti}_3\text{Al+Nb}$ plates were conducted by hot pressing Cu and SiC plates or Cu and $\text{Ti}_3\text{Al+Nb}$ plates together under the same conditions as described above.

The hot-pressed samples were sectioned, polished, and examined by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS).

RESULTS AND DISCUSSION

Cu/SiC reaction at 1273 K

Figure 1 shows a Cu/SCS-6 composite hot pressed at 1273 K for 2 hr. The outer double-layer carbon-rich coating on SCS-6 fibers has been broken at several places. Detachment of the outer coating from the SiC fiber can be seen at several locations. Copper has penetrated the outer carbon coating and reacted with SiC at a few locations. Because a single fiber is being pressed between two

metal plates, the localized pressure on the fiber must be very high at the beginning, i.e., before the two Cu plates are in contact with each other. Initially, it was thought that the damage to the outer coating was probably due to this high localized pressure at the beginning of hot pressing. However, parallel experiments in which a single SCS-6 fiber was hot-pressed between two Ti_3Al plates at the same temperature but with an applied pressure much higher (100 - 110 MPa) did not reveal any damage to the outer carbon coating, as shown in figure 2. It appears that the damage to the outer coating and the SiC fiber during hot pressing must be related to chemical interaction between Cu and the SiC fiber.

A silicon carbide fiber without any outer carbon coating (SCS-0 fiber) reacted extensively with Cu after hot pressing at 1273 K for 2 hr, as shown in figure 3. This shows that Cu is not chemically compatible with SiC.

Reaction of Cu with CVD SiC was further studied by hot pressing a Cu/CVD SiC plate sandwich at 1273 K. Initial pressure applied was about 10 MPa. However, after 10 minutes, the pressure became zero and attempts to maintain a constant pressure of 10 MPa were unsuccessful. The hot-pressing run was therefore stopped after 30 minutes. After cooling, spherical Cu globules could be seen inside the hot-press die, suggesting that a molten reaction product formed during hot pressing. A part of the Cu/SiC sandwich was still intact after hot pressing. Chemical analyses of two of the solidified globules gave the following compositions: Cu-6.3 a/o Si and Cu-9 a/o Si. Note that the composition Cu-9 a/o Si corresponds to the liquidus composition on the Cu-rich side of the Cu-Si phase diagram at 1273 K (ref. 3).

The remaining portion of the Cu/CVD SiC sandwich that was hot pressed at 1273 K for 30 min was cross sectioned and examined by SEM. The cross section, figure 4, shows a thick reaction zone between Cu and SiC. The reaction zone is a mixture of metallic Cu (probably a Cu-Si alloy) and fine, dark particles. X-ray dot maps (figure 5) for C, Cu, and Si show these dark particles to be rich in carbon but depleted in Cu and Si. These dark particles are probably free carbon.

The reaction products between Cu and CVD SiC were further characterized by hot pressing a thin (20 μm) Cu foil on to a CVD SiC plate at 1273 K for 15 min. The Cu foil completely reacted and no trace of Cu was observed after hot pressing. Figure 6 compares the EDS spectra of the surface for reacted and as-received SiC, obtained under the same SEM operating conditions. The reacted surface contains Cu, Si, and C. The C/Si peak height ratio for the reacted SiC surface is much higher than that of the as-received

SiC. Because carbon is not soluble in either Cu or SiC, large carbon peak on the reacted surface must be due to free carbon on the surface.

Cu/SiC reaction at 1223 K

No damage either to the outer carbon-rich coating or the SiC fiber itself occurred for Cu/SCS-6 composite hot pressed at 1223 K for 2 hr, shown in figure 7. In most of the areas, a clean fiber-Cu interface was obtained (Fig. 7b). However, in a few areas some reaction could be observed (Fig. 7c). In spite of this reaction, the double-layer outer carbon coating was still intact and not separated from the SiC fiber.

Some reaction between Cu and CVD SiC plate was also observed at 1223 K, as shown in figure 8. The extent of reaction at this temperature is much lower compared to that at 1273 K, although morphology of the reaction product is similar to that at 1273 K. More important, the reaction product was not molten at 1223 K.

Interaction of Cu with SiC fibers: reaction mechanism

The results from this study have clearly shown that Cu is not chemically compatible with SiC. Chemical reaction between Cu and SiC results in the formation of a Cu-Si solution, liquid or solid depending on temperature, along with free carbon, i.e.,



As discussed below, the above reaction is also thermodynamically feasible. Unless otherwise stated, the relevant thermodynamic data were taken from the JANAF Thermochemical TABLES (ref. 4) and the compilations by Barin and Knacke (ref. 5).

Because the solubility of carbon in Cu is extremely low (ref. 6), Cu would react with SiC by forming free carbon and dissolving Si in Cu, i.e., by Reaction [1], until the activity of Si in Cu becomes equal to the equilibrium Si activity for the reaction,



which is 2.5×10^{-3} (with respect to solid Si) at 1273 K. Thus, at 1273 K, Cu will continue to react with SiC by Reaction [1] until the Si activity in Cu becomes equal to 2.5×10^{-3} .

It will be of interest to see if an Si activity of 2.5×10^{-3} corresponds to a Cu-Si liquid at 1273 K. From the Cu-Si binary

phase diagram (ref. 3) the Si concentration corresponding to the liquidus composition on the Cu-rich side of the Cu-Si phase diagram is 9 at. pct. Thus, the minimum Si concentration required for a Cu-Si liquid formation at 1273 K is 9 a/o. The Si activity in this melt must be lower than or equal to the equilibrium Si activity for Reaction [2], i.e., 2.5×10^{-3} , if a melt is to form by the reaction of Cu with SiC. The activity of Si (with respect to solid Si) in a Cu-9a/oSi melt at 1273 K, obtained by extrapolating Nikitin's (ref. 7) activity data at 1673 K with the assumption of a regular solution model, is about 2.9×10^{-3} which is nearly the same as the equilibrium Si activity for Reaction [2] at this temperature. Thus, a Cu-Si liquid is likely to form by the reaction of Cu with SiC at 1273 K.

Calculations similar to those described above can also be made to examine if a liquid can form by the reaction of Cu with SiC at 1223 K. The equilibrium Si activity (with respect to solid Si) for Reaction [2] at 1223 K is 1.88×10^{-3} . The minimum Si concentration necessary for the formation of a Cu-Si melt at 1223 K, i.e., the Si concentration corresponding to the liquidus composition on the Cu-rich side of the Cu-Si phase diagram, is about 11.8 a/o. The activity of Si (with respect to solid Si) for a melt of this composition at 1223 K, again obtained by extrapolation of Nikitin's data at 1673 K with the assumption of regular solution model, is 2.18×10^{-2} , which is an order of magnitude higher than the equilibrium Si activity (1.88×10^{-3}) for Reaction [2] at this temperature. Thus, a Cu-Si liquid cannot form by the reaction of Cu with SiC at 1223 K. At this temperature Cu would react with SiC to form a Cu-Si solid solution and free carbon.

The conclusions from the thermodynamic analysis, i.e., Cu would react with SiC to form a Cu-Si melt at 1273 K but not at 1223 K, are clearly consistent with the results from the present study.

Although Cu is not chemically compatible with SiC, Cu is inert to carbon or graphite (ref. 6). The question, then, arises why does Cu damage the outer carbon-rich coating on SCS-6 fibers during hot pressing at 1273 K? The answer probably lies in the microstructure and microcomposition of this carbon-rich coating. The outer carbon-rich coating contains a small amount of Si (ref. 8), presumably present as fine silicon carbide particles. Copper can react with these silicon carbide particles resulting in the formation of a Cu-Si melt which can penetrate the coating in localized areas during hot pressing and cause damage to the coating. Once the outer carbon coating is cracked, Cu because of its plasticity at high temperatures can flow through these cracks during hot pressing and come in contact and react with the

SiC fiber.

The fact that no damage to the outer coating was observed at 1223 K strongly suggests that the formation of a Cu-Si melt due to the reaction of Cu with fine SiC particles in the outer coating is responsible for the damage to the outer coating. As discussed earlier, Cu-SiC reaction results in the formation of a melt at 1273 K but not at 1223 K.

Reaction of Cu with Ti_3Al+Nb

Cu/ Ti_3Al+Nb diffusion couples completely melted after heat-treatment at 1273 K as well as at 1223 K. This necessitates the need for a reaction barrier between Cu and Ti_3Al . One possible reaction barrier is Nb. The solubility of Nb in solid Cu is negligible (ref. 9). The solubility of Cu in Nb appears to be very small, less than 1 at. % (ref. 9), at 1273 K and is negligible at 1073 K, the anticipated use temperature for SiC/ Ti_3Al+Nb composite. Thus, Nb can be an effective reaction barrier between Cu and Ti_3Al+Nb provided it does not react excessively with Ti_3Al+Nb .

Figure 9 shows the cross section of a Cu/ Ti_3Al+Nb diffusion couple heat treated at 1273 K for 2 hr with an interlayer of Nb. As expected, an interlayer of Nb prevented the reaction between Cu and Ti_3Al+Nb at 1273 K. Reaction of Nb with Ti_3Al+Nb has resulted in an interfacial reaction zone, 10-12 μm thick. From electron probe microanalysis the average composition of this reaction zone was determined to be 51%Ti, 31%Nb, 18%Al (all in atomic percent), which corresponds to a β -phase Nb-Ti-Al alloy (ref. 10).

The thickness of the interfacial reaction zone between Nb and Ti_3Al+Nb remains more or less the same after further heat treatment at 1073 K, the intended use temperature for Ti_3Al/SiC composites, for 100 hr, as shown in figure 10. Thus, once the composite has been fabricated with a Nb interlayer, further reaction between this interlayer and the Ti_3Al+Nb matrix at the use temperature proceeds at a very slow rate and may not be of much concern.

SUMMARY

The chemical compatibility issues related to the use of Cu as an interfacial layer for SiC fiber reinforced Ti_3Al+Nb composite were examined. Copper reacted with SiC at 1273 K to form a Cu-Si liquid and free carbon. On the other hand, at 1223 K, although Cu still reacted with SiC, no molten reaction product formed at this temperature. These results are consistent with the thermodynamic analysis for the Cu-SiC reaction.

Hot pressing of a Cu/SCS-6 composite at 1273 K resulted in cracking and damage of the outer carbon-rich coating of the fiber, which is believed to be due to the formation of a liquid by reaction of Cu with fine SiC particles in the outer coating of the fiber. Cracking of the fiber allowed Cu to flow to the SiC-carbon coating interface and react with SiC. No such damage to the outer fiber coating was observed for a Cu/SCS-6 composite hot pressed at 1223 K, although some reaction products were observed near the Cu/SCS-6 interface.

Copper reacted with $\text{Ti}_3\text{Al}+\text{Nb}$ at both 1273 and 1223 K to form a molten reaction product. An interlayer of Nb between Cu and $\text{Ti}_3\text{Al}+\text{Nb}$ prevented the reaction between the two. There was some reaction between Nb and $\text{Ti}_3\text{Al}+\text{Nb}$ at the fabrication temperature; however, the rate of reaction appears to be very slow at the use temperature and may not be of much concern.

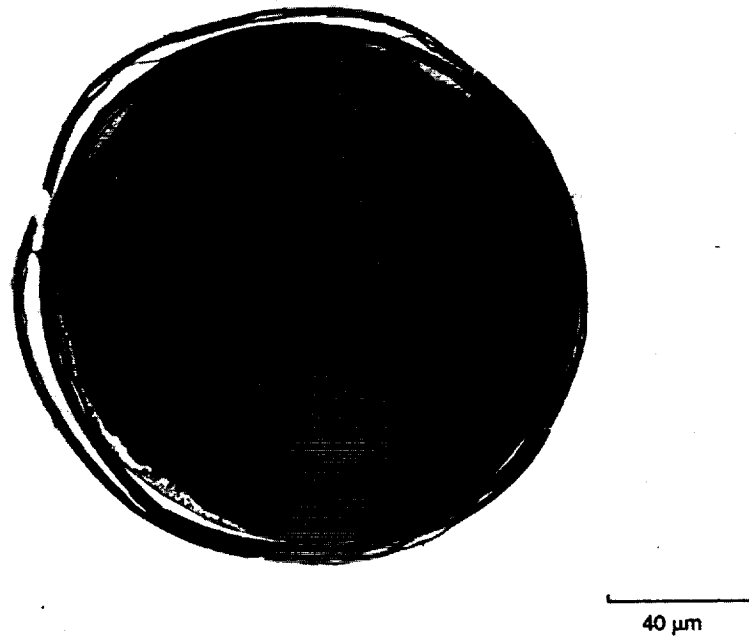
CONCLUSIONS

Chemical compatibility considerations dictate that the $\text{Ti}_3\text{Al}+\text{Nb}/\text{SCS-6}$ composite with a Cu interfacial layer should be processed, i.e., hot-pressed or HIPed, at 1223 K instead of 1273 K, which is the normal processing temperature for this composite system. A lower processing temperature is required in order to avoid damage/cracking of the outer carbon-rich coating of the SCS-6 fiber. Furthermore, the Cu-coated SCS-6 fiber must be further coated with a suitable diffusion barrier, such as Nb, to prevent excessive reaction between Cu and Ti_3Al at the processing temperature.

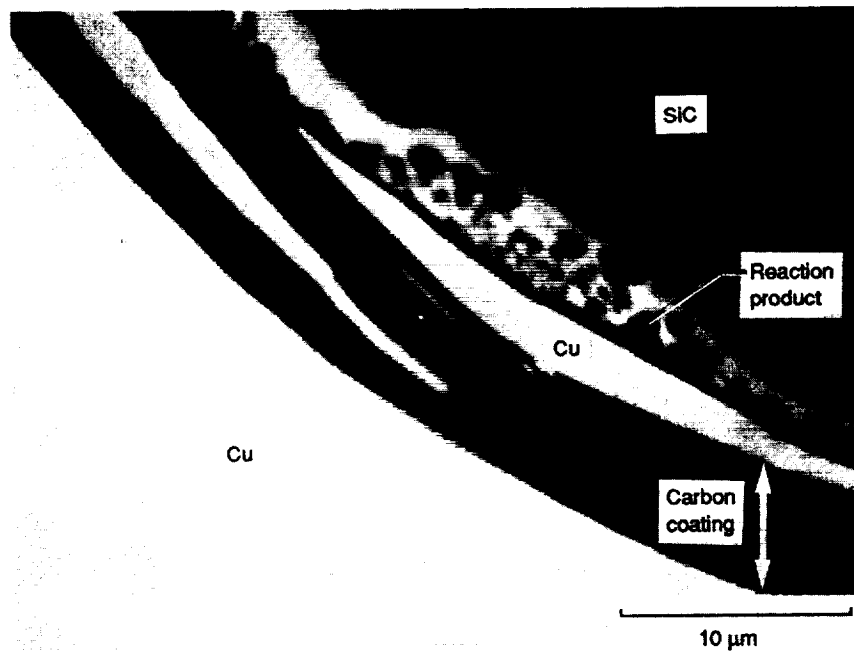
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(a) Overall cross section.



(b) Cu/fiber interface at higher magnification.

Figure 1.—SCS-6 fiber hot pressed between two Cu plates at 1273 K for 2 hr.

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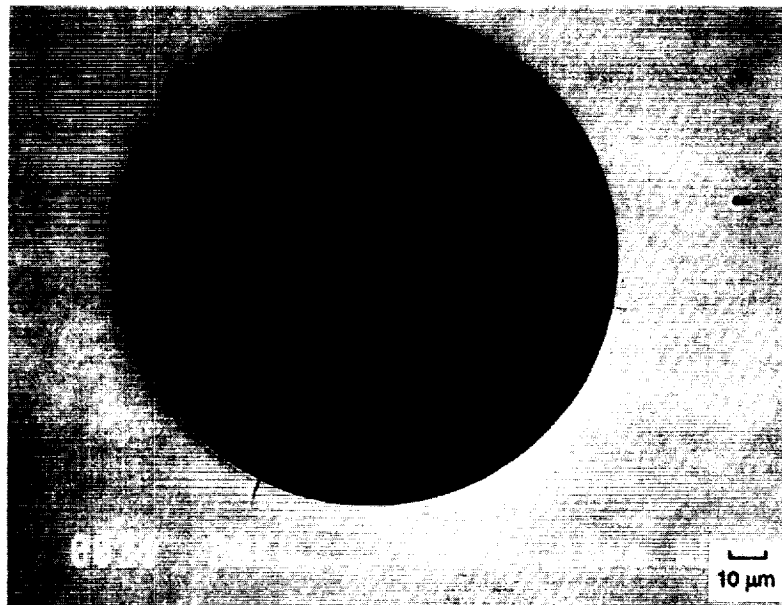
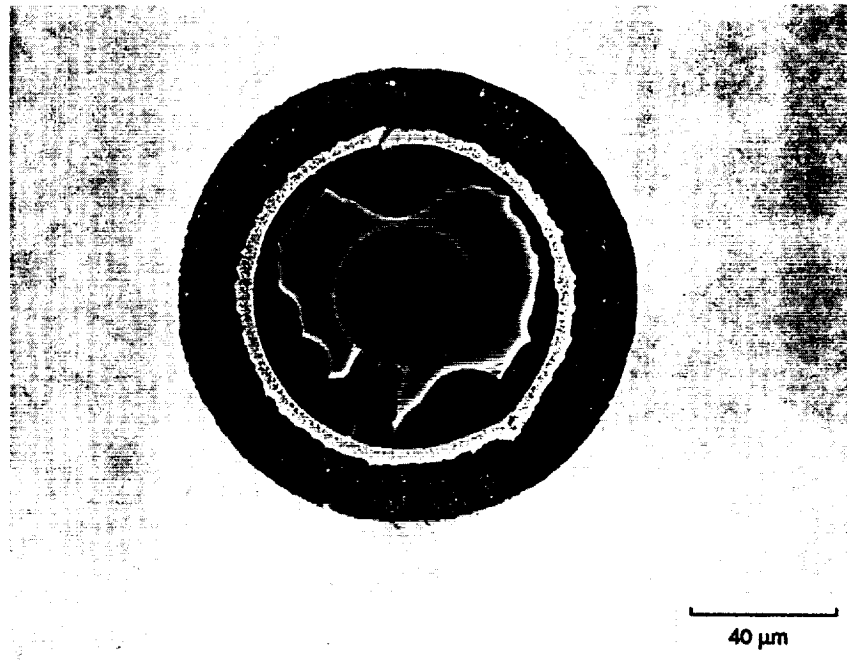


Figure 2.—A SCS-6 fiber hot pressed between two Ti_3Al plates under 100 MPa at 1273 K for 2 hr.

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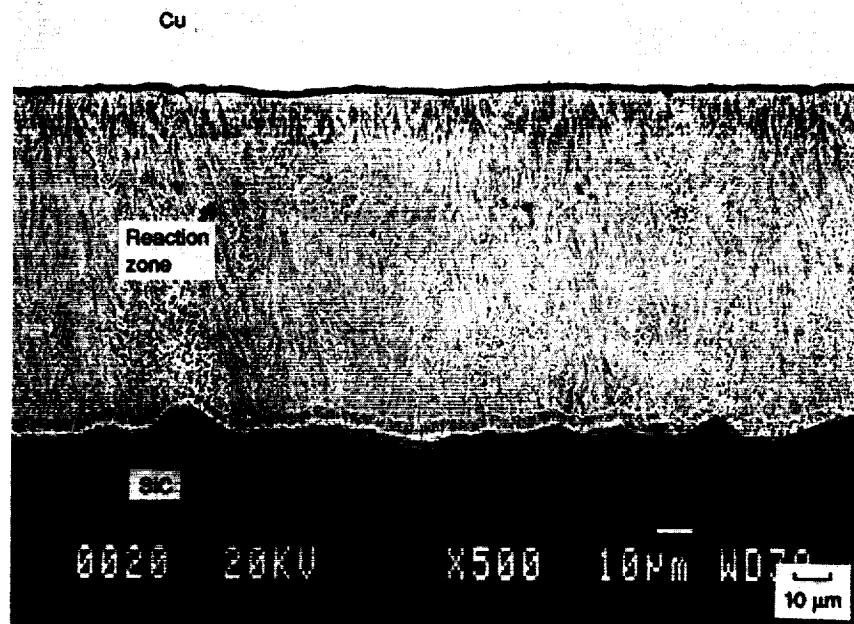
(a) Overall cross section.



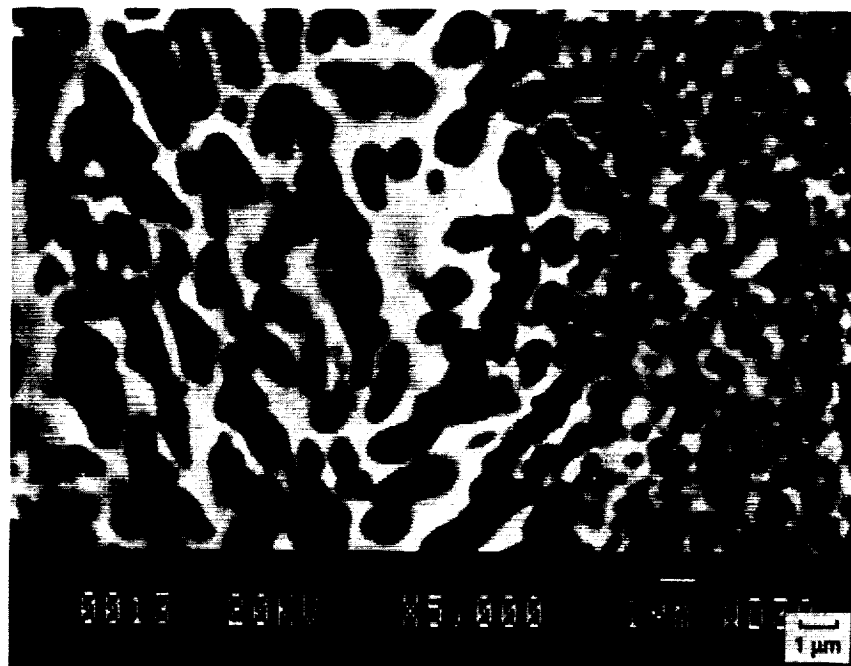
(b) Cu/fiber interface at higher magnification.

Figure 3.—SCS-0 fiber hot pressed between two Cu plates at 1273 K for 2 hr.

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(a) Overall cross section.



(b) Magnified view of the reaction zone.

Figure 4.—Cu/CVD SiC plate hot pressed at 1273 K for 30 min.

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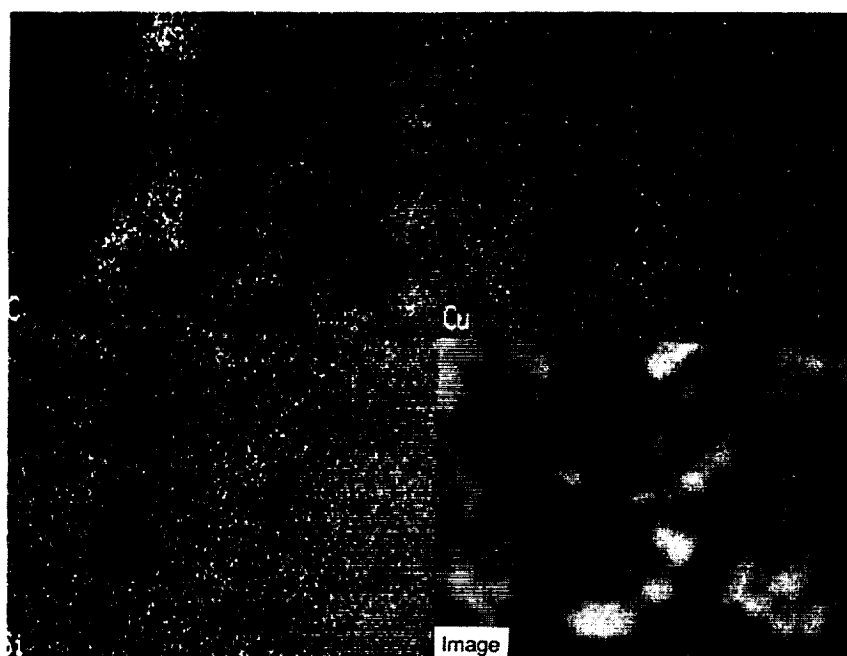
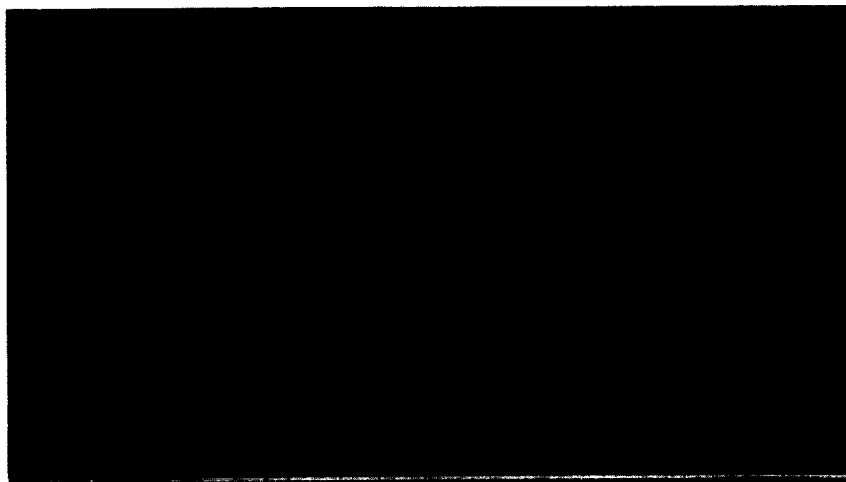
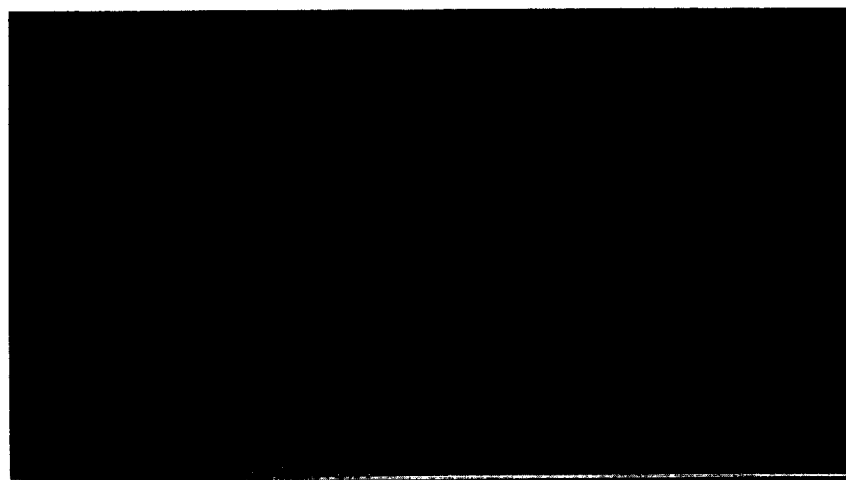


Figure 5.—X-ray dot maps for Cu, C, and Si for an area in the reaction zone for Cu/CVD SiC sandwich hot pressed at 1273 K for 30 min.

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(a) As-received.



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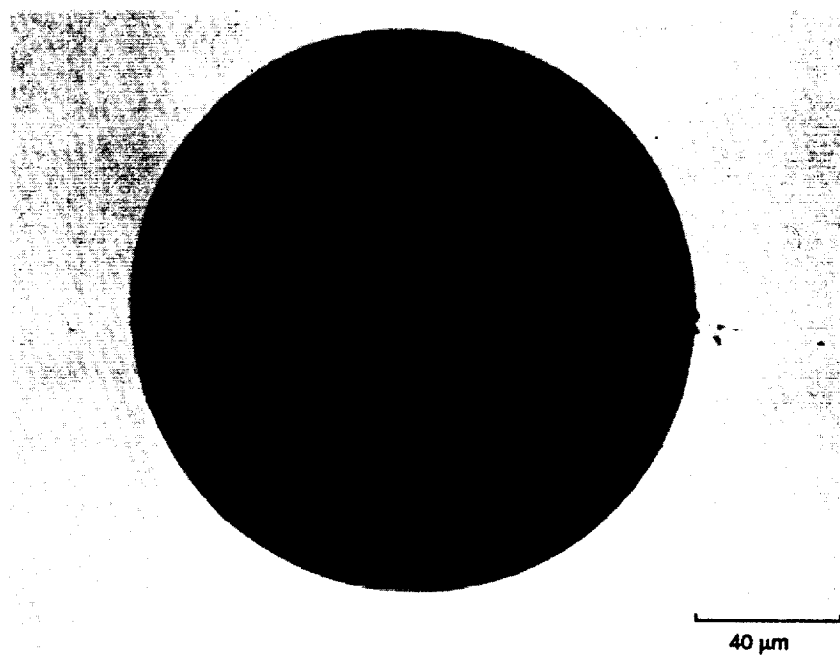
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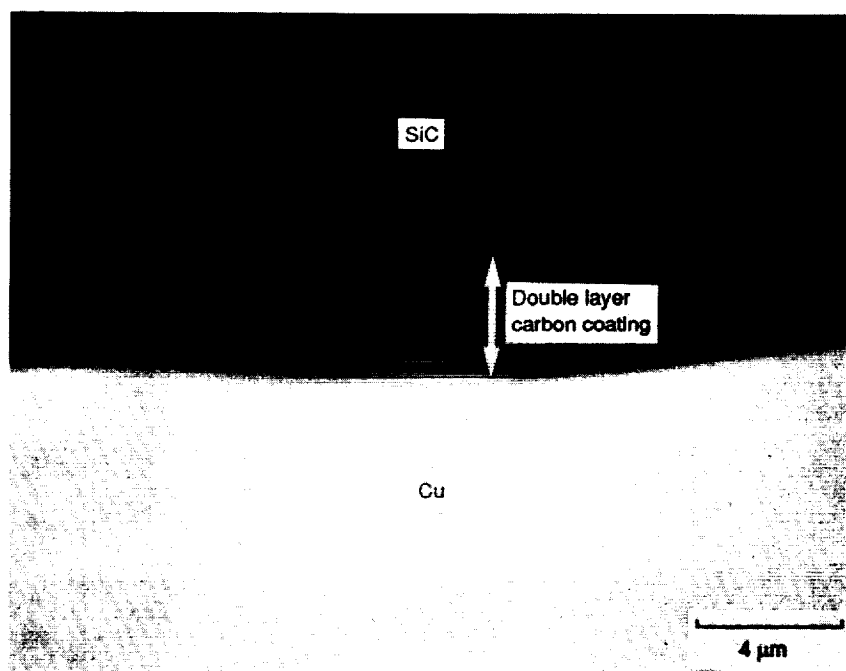
(b) Reacted with a thin Cu foil at 1273 K for 15 min.

Figure 6.—EDS spectra of CVD SiC surface.

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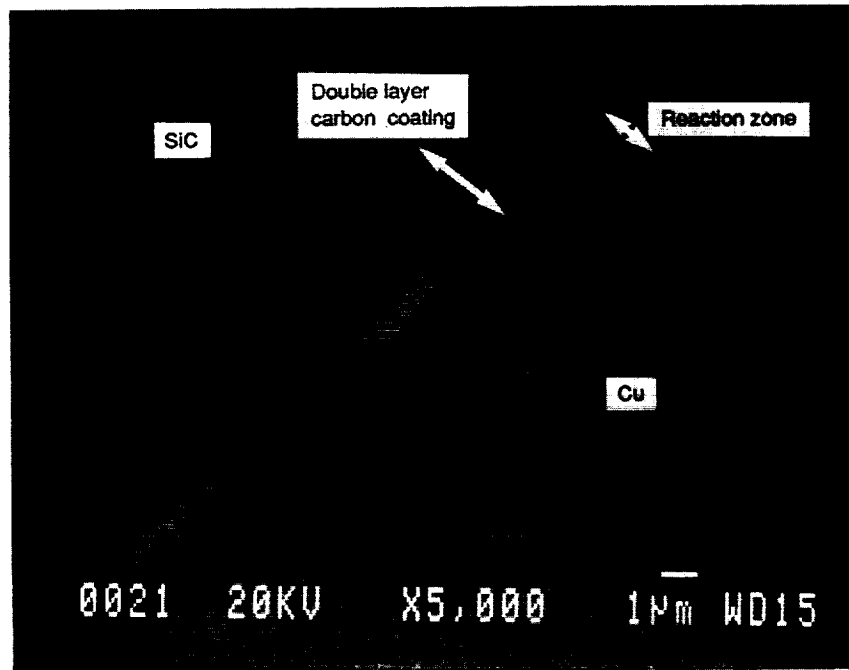
(a) Overall cross section.



(b) An area of Cu/fiber interface showing no reaction.

Figure 7.—SCS-6 fiber hot pressed between two Cu plates at 1273 K for 2 hr.

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(c) An area of Cu/fiber interface showing some reaction.

Figure 7.—Concluded.

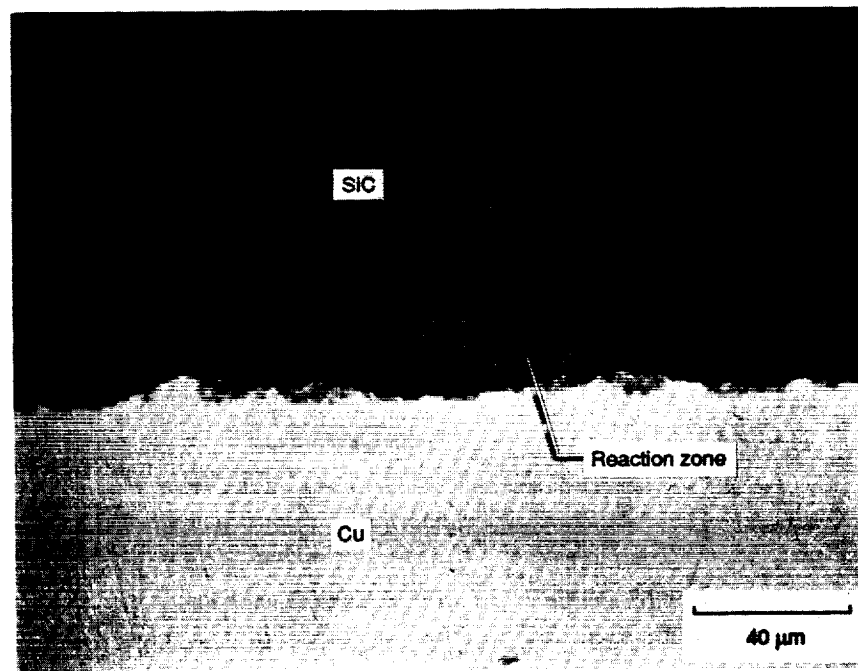


Figure 8.—Cu/CVD SiC plate hot pressed at 1223 K for 2 hr.

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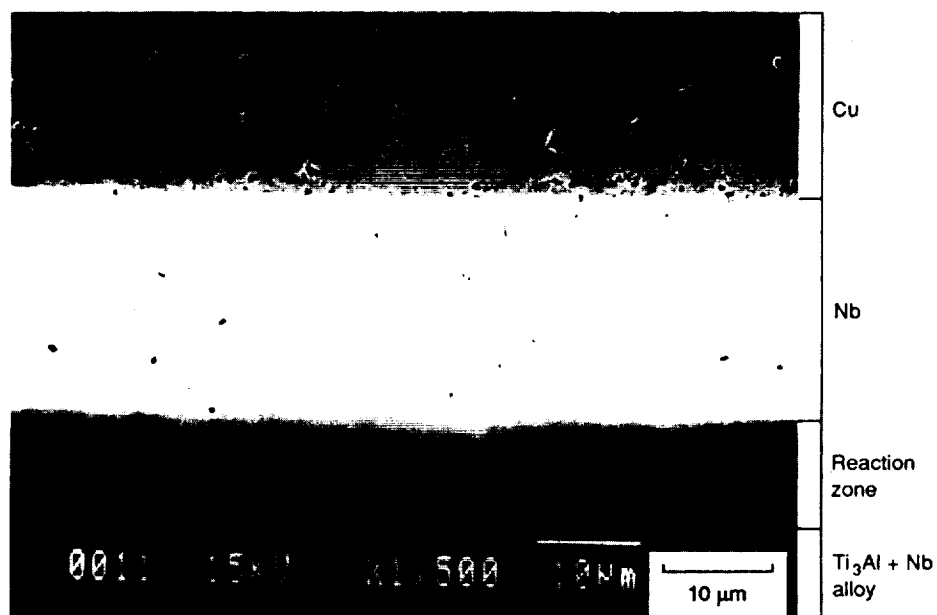
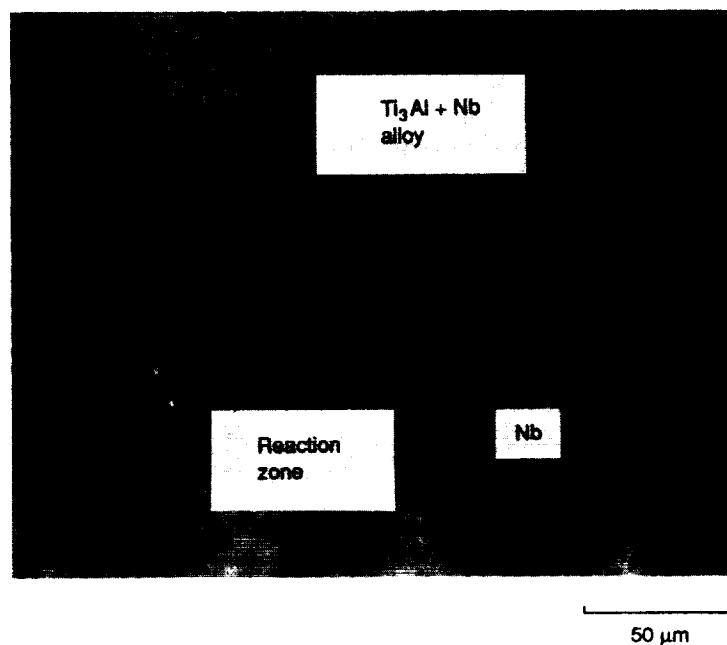
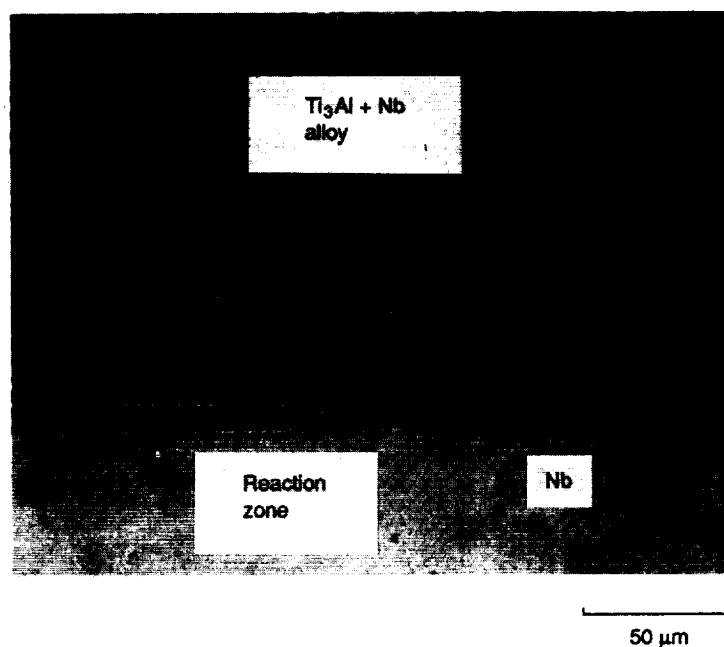


Figure 9.—Cross section of Cu/Nb/Ti₃Al + Nb sandwich hot pressed at 1273 K for 2 hr.

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(a) Hot pressed at 1273 K for 2 hr.



(b) Hot pressed at 1273 K for 2 hr followed by annealing for 100 hr at 1073 K.

Figure 10.—Cross section of $\text{Ti}_3\text{Al} + \text{Nb/Nb}$ sandwich.



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